Multiply reconfigurable 'plug and play' molecular logic *via* self-assembly†

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A substantial set of ion-driven molecular logic gates are implemented in turn by arranging the association between easily available lumophores and receptors in detergent micelles.

The concept of 'plug and play' adds greatly to the convenience of semiconductor electronic devices, where the addition of new modules directly enables new functions.[1] Now we demonstrate this concept for molecular logic devices[2,3] so that different logic configurations arise upon the straightforward addition of new modules under self-assembly conditions.[4] PASS 0,[5] PASS 1,[5] YES, NOT, OR, AND gates are implemented with the minimum of organic synthesis effort.

Molecular logic continues to show significant conceptual progress (reconfiguring,[6] small-scale integration,[7] numeracy,[3o,8] gaming[9]) and applications of wide scope.[3h,5,10] It is important to demonstrate simpler ways of achieving molecular logic so that more opportunities arise for conceptual development.

It has been clear for some time that self-assembled 'lumophore–receptor' systems could be profitable for sensing and logic.[11] Sensing ensembles[12] have been some of the best realizations. Detergent micelles also allow self-assembly of lumophores and potential receptors.[13] Pallavicini's[14] luminescent 'off–on–off' system[15] is a fine example which exploits photoinduced electron transfer (PET).[16] Since PET-based luminescent systems are necessarily modular,[11] now we can develop a set of molecular logic gates serially.

Though the physical electronic symbol may not reflect it at first sight, PASS 0 is perhaps the simplest of Boolean logic operations[17] (Fig. 1). To some, it would even appear trivial. Nevertheless, it has been employed as a tag in molecular computational identification.[5] An aqueous solution of the neutral detergent Triton X-100 above its critical micellar concentration, when interrogated with 450 nm excitation and 625 nm observation, shows no emission whether the H^+ input is 'low' or 'high' (Table 1) since it is devoid of a suitable chromophore. This truth table corresponds to a PASS 0 logic device, which is driven by H^+ input.

Addition of the hydrophobic tris(2,2′-bipyridyl)Ru(II) complex **1**[18] at 6.7×10^{-6} M to the Triton X-100 solution enables the lumophore to reside within the detergent micelles (Fig. 1). Interrogation as before produces a 'high' emission signal whether H^+ input is 'low' or 'high' (Table 1), since there are no basic centres to engage H^+ under these conditions. This emulates PASS 1 logic. Any fluorescent or luminescent dye would satisfy this requirement, but the relatively long emission lifetime of **1** (several hydrophobic tris(2,2′-bipyridyl)Ru(II) complexes give an average value of 200 ns)[19] enables it to perform the subsequent logic operations better than shorter-lived counterparts.

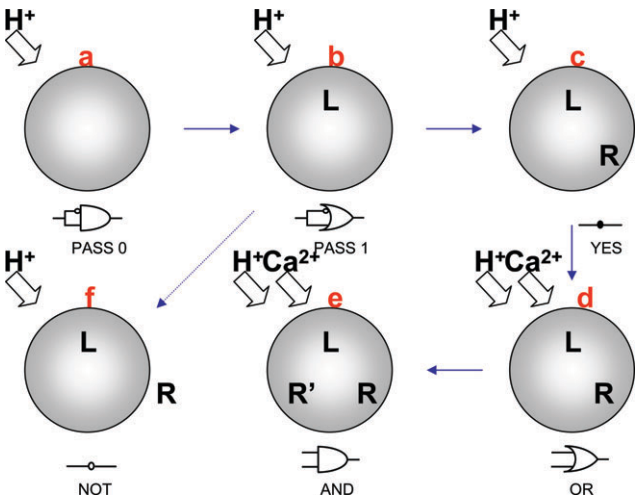
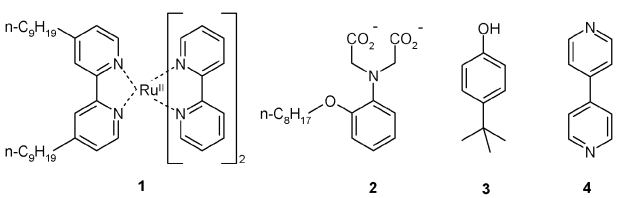


Fig. 1 Schematic representation of the micellar solutions containing various combinations of lumophores and receptors. These receive inputs of various combinations of H^+ and Ca^{2+}. Emission at 625 nm, when excited at 450 nm, is the observed output. Physical electronic symbols of the logic gates that each of these assemblies produce are also given. The solutions are undeaerated in order to maximize the convenience of the experiments.



Further addition of receptor **2** allows most of the micelles occupied by **1** to co-include **2**.[20] Receptor **2** is conveniently prepared from 2-nitrophenyl-*n*-octyl ether (a common plasticizer for ion-selective electrode membranes)[21] by hydrogenation (Pd/C), *N*,*N*-dialkylation ($BrCH_2CO_2Me$–K_2CO_3) and hydrolysis (KOH).‡ Interrogation as before at pH = 12 gives

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Table 1 Truth tables for a series of molecular logic gates self-assembled in detergent micelles[a]

System	$Input_1$	$Input_2$	Output	Logic
TX	0 (10^{-12} M H^+)	—	0 (low, 0.0)	PASS 0
TX	1 (10^{-2} M H^+)	—	0 (low, 0.0)	PASS 0
TX + **1**	0 (10^{-12} M H^+)	—	1 (high, 57)	PASS 1
TX + **1**	1 (10^{-2} M H^+)	—	1 (high, 63)	PASS 1
TX + **1** + **2**	0 (10^{-12} M H^+)	—	0 (low, 6)	YES
TX + **1** + **2**	1 (10^{-2} M H^+)	—	1 (high, 44)	YES
TX + **1** + **2**[b]	—	0 (0.0 M Ca^{2+})	0 (low, 7)	YES
TX + **1** + **2**[b]	—	1 (0.2 M Ca^{2+})	1 (high, 32)	YES
TX + **1** + **2**	0 (10^{-8} M H^+)	0 (0.0 M Ca^{2+})	0 (low, 9)	OR
TX + **1** + **2**	0 (10^{-8} M H^+)	1 (0.2 M Ca^{2+})	1 (high, 30)	OR
TX + **1** + **2**	1 (10^{-4} M H^+)	0 (0.0 M Ca^{2+})	1 (high, 36)	OR
TX + **1** + **2**	1 (10^{-4} M H^+)	1 (0.2 M Ca^{2+})	1 (high, 34)	OR
TX + **1** + **3**	0 (10^{-12} M H^+)	—	0 (low, 10)	YES
TX + **1** + **3**	1 (10^{-8} M H^+)	—	1 (high, 62)	YES
TX + **1** + **2** + **3**	0 (10^{-12} M H^+)	0 (0.0 M Ca^{2+})	0 (low, 4)	AND
TX + **1** + **2** + **3**	0 (10^{-12} M H^+)	1 (0.2 M Ca^{2+})	0 (low, 11)	AND
TX + **1** + **2** + **3**	1 (10^{-8} M H^+)	0 (0.0 M Ca^{2+})	0 (low, 15)	AND
TX + **1** + **2** + **3**	1 (10^{-8} M H^+)	1 (0.2 M Ca^{2+})	1 (high, 36)	AND
SDS + **1** + **4**	0 (10^{-8} M H^+)	—	1 (high, 52)	NOT
SDS + **1** + **4**	1 (10^{-2} M H^+)	—	0 (low, 28)	NOT

[a] 2×10^{-3} M Triton X-100 (TX) or 4×10^{-2} M SDS aqueous solution with a combination of 6.7×10^{-6} M **1**, 10^{-3} M **2**, 10^{-3} M **3** and 10^{-3} M **4** as indicated above. The outputs are luminescence quantum yields (ϕ_{Lum}) given as $10^3\phi_{Lum}$ values. The 'low' and 'high' levels of inputs are determined by the ion-binding strengths of the various receptors **2**–**4** in the micellar media. For instance, a 'high' level of H^+ input requires a pH value at least 1 unit lower than the operational pK_a value of the receptor component of the logic gate. Cases without receptors employ the levels used in related systems containing receptors. The 'low' and 'high' levels of outputs are determined by setting thresholds so that the predicted truth table is reasonably attained. A $10^3\phi_{Lum}$ value of 20 is chosen as the threshold for the OR gate. A $10^3\phi_{Lum}$ value of 25 is chosen as the threshold for the AND gate. [b] pH = 8.

a 'low' luminescence output due to intramicellar PET from the aromatic amine to **1**.[13] In contrast, the emission output is enhanced by a factor of 7.0 at pH = 2 since the quenching effect of the amine is negated by its protonation.[22] So the emission output follows the H^+ input[14] (Table 1), corresponding to H^+-driven YES logic. The analysis of the output–input profile[23] gives the H^+-binding constant (pK_a) of **2** as 5.8.

The micellar solution containing lumophore **1** and receptor **2** can also be interrogated at 'low' (0 M) and 'high' (0.2 M) inputs of Ca^{2+} at pH = 8. Ca^{2+}-driven YES logic is seen (Table 1) with a Ca^{2+}-induced enhancement factor of 4.5 and a Ca^{2+}-binding constant (log β) of 1.6.

It is then logical to optically interrogate the aqueous Triton X-100, **1** and **2** system with both H^+ and Ca^{2+} inputs since the receptor **2** responds to both. Such non-selective receptors have led to OR logic in intramolecular cases.[24] As Table 1 shows, a 'high' luminescence output is seen in all conditions except when both H^+ and Ca^{2+} inputs are 'low', provided that reasonable input and output thresholding is applied. H^+, Ca^{2+}-driven OR logic is the result. The Ca^{2+}-binding constant of 1.6 and pK_a of 5.8 determined above are applicable here.

H^+-receptors other than **2** can be profitably examined. *t*-Butylphenol (**3**) in its deprotonated form fits the bill. Phenolates, as opposed to phenols, serve as electron donors to excited tris(2,2′-bipyridyl)Ru(II) complexes.[25] Optical interrogation of the aqueous solution of Triton X-100, **1** and **3** at pH = 12 gives a 'low' emission output. In contrast, pH = 8 gives a luminescence enhancement factor of 6.0. Corresponding intramolecular cases are known.[26] The pK_a value of **3** under these conditions is 9.9.

The substantially different pK_a values of **2** and **3** allows us to choose a pH range (8–12) so that **2** loses its pH sensitivity and only responds to Ca^{2+}. We now have a suitably selective pair of receptors, which, in non-micellar PET systems without self-assembly, produces AND logic.[2,3g,27] An aqueous micellar solution of **1**, **2** and **3** allows a substantial fraction of the micelles containing **1** to also contain **2** and **3**.[20] Excitation at 450 nm and observation at 625 nm gives a 'high' emission output only when both H^+ and Ca^{2+} inputs are 'high', subject to reasonable thresholds being used (Table 1), corresponding to AND logic. A Ca^{2+}-binding constant of 1.5 and pK_a of 10.3 are found. These are reasonably close to the values obtained for the log $\beta_{Ca^{2+}}$ for **2** and the pK_a of **3** separately.

Finally, we revisit frame (b) in Fig. 1. Instead of electrically neutral Triton X-100, we now turn to anionic dodecylsulfate micelles (SDS) with Na^+ counter-ions. Complex **1** associates with SDS micelles electrostatically as well as hydrophobically. Now we evolve frame (b) to frame (f) in Fig. 1 by adding 4,4′-bipyridyl (**4**) to act as the receptor for H^+. Though **4** itself may not associate with SDS micelles, diprotonated **4** would associate electrostatically. Intramicellar PET from tris(2,2′-bipyridyl)Ru(II) to *N*,*N*-dimethylated **4** in SDS has been known for a long time.[28] A similar PET process from **1** to diprotonated **4** can be assigned as the cause of significant luminescence quenching by a factor of 1.8 at pH = 2 (as compared to the emission at pH = 8). The operational pK_a value of **4** is 4.8 (Table 1). Since 'high' H^+ input produces 'low' emission output and *vice versa*, we have NOT logic here.

In conclusion, all the single-input, single-output Boolean logic operators and two important cases of the double-input, single-output versions can be produced by simple addition of lumophores and receptors into aqueous micellar solutions. The micellar self-assembly approach is very convenient, though the intensity ratios of the 'high' and 'low' output states deserve improvement in future studies. This approach complements the use of luminescent, but covalently bound, switching systems for the examination of micellar environments.[29]

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Notes and references

‡ Methyl ester of **2**; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 6.75–6.92 (m, Ar*H*, 4H), 4.13 (s, NCH_2, 4H), 3.92 (t, OCH_2, 2H), 3.68 (s, OCH_3, 6H), 1.88 (m, OCH_2CH_2, 2H), 1.53 (m, $OCH_2CH_2CH_2$, 2H), 1.39 (m, $CH_2(C_4H_8)CH_3$, 8H), 0.98 (t, $O(C_7H_{14})CH_3$, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): 172.5, 151.2, 139.3, 122.7, 120.5, 119.3, 112.9, 70.1, 69.0, 55.0, 53.7, 32.2, 30.5, 29.7, 26.5, 23.1, 14.6. MS(EI): m/z = 365.2228 (M^+), 306 ($M^+ - CO_2CH_3$). Calculated m/z for $C_{20}H_{31}O_5N$ = 365.2202.

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